Optical properties and energy band parameters of luminescent $CaMoO_4$:Bi ceramics

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Abstract. We studied the role of intrinsic defects of matrix and Bi dopant in the formation of optical properties and energy structure of $CaMoO_4$:Bi ceramic. Non-elementary luminescence was detected in a pure $CaMoO_4$ matrix due to radiative transitions in intrinsic vacancy-type defects, which are associated with non-stoichiometry in calcium. The experiment showed that Bi ions act as quenchers of luminescence.

1. Introduction

Scheelite-like oxides of the ABO_4 type are promising research objects due to the relative ease of doping and, as a result, the variety of chemical composition and functional characteristics of the compounds obtained. Scheelite-like compounds are perspective materials for applications in lasers, optoelectronics, photonics, etc [1].

2. Samples and methods

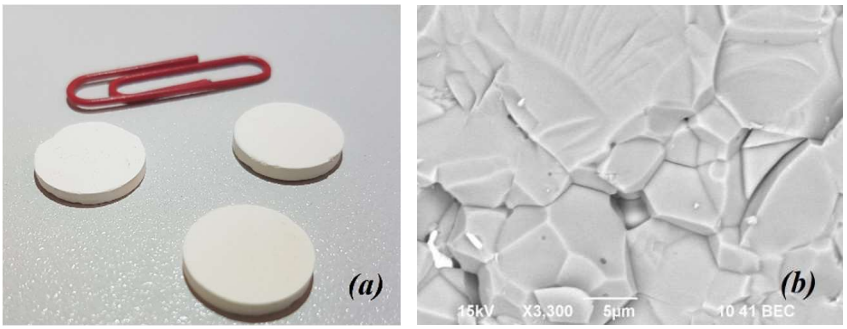

Figure 1 (a, b). (a) Samples of $CaMO_4$:Bi; **(b)** SEM image of $Ca_{0.7}Bi_{0.2}MoO_4$ ceramics.

Synthesis of $CaMoO_4$:Bi was made in terms of the standard ceramics models of for Bi_2O_3, MoO_3, $CaCO_3$ stoichiometric compounds grinded in the agate mortar box with the use of alcohol as homogenizer and annealed in 500-700°C temperature range (fig. 1, a). Samples were certificated by using x-ray fluorescence analyzer (Bruker Advance D8 diffractometer, VÅNTEC detector, CuK_α radiation, Ni-filter, θ/θ geometry). Elementary cell parameters were calculated within structureless way in Fullprof suite.

Microstructure analysis of sintered samples was made with the use of raster electron microscope JEOL JSM 6390LA that includes an energy dispersive microanalyzer JED 2300 (fig. 1, b).

Reflection spectra of $CaMO_4$:Bi were obtained on a Perkin Elmer Lambda 35 spectrometer with a spectral step of 1 nm and a slit of 2 nm. Using the Kubelka-Munk model provides the conversion of the initial experimental data to the absorption spectra. In accordance with Kubelka-Munk equation:

$$F(h\nu) = \frac{(1-R)^2}{2R} \quad (1)$$

where F(hν) is the Kubelka-Munk function that is directly proportional to the absorption coefficient, R – spectral reflection coefficient. At the same time, the Tauc power-law expression was used for determining of energy gap [2, 3]:

$$\alpha(h\nu) \cdot h\nu = A \cdot (h\nu - E_g)^n \quad (2)$$

where A is a constant, E_g is the energy gap, n is the exponent that determines the type of interband transitions (1/2; 3/2; 2 and 3 for direct and indirect allowed and forbidden transitions respectively). Luminescent properties were investigated on a Perkin Elmer LS 55 spectrometer. The emission was registered in the 1.8-3.5 eV spectral range after the excitation by photons with energies of 4-6 eV (this region is most effective for the exciton generation).

3. Results and discussion

3.1 Reflection spectra

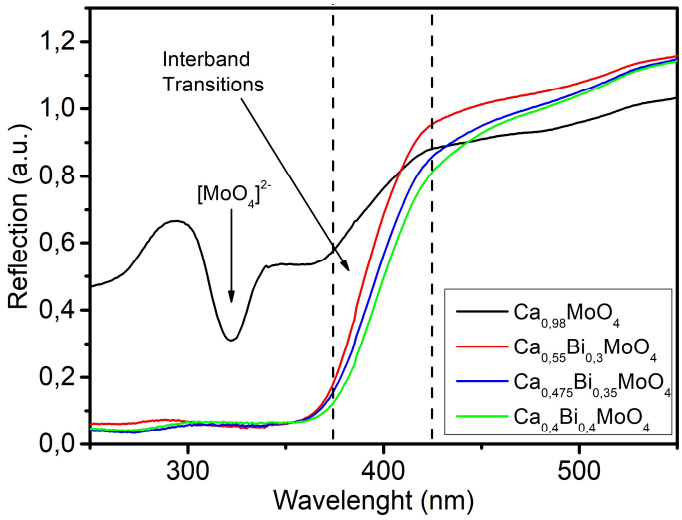

Figure 2. Reflection spectra for $Ca_{1-3x}Bi_{2x}\Phi_xMoO_4$. The dotted lines show the region that was used for obtaining the absorption spectra. Arrow shows a MoO_4^{2-} anion complex for undoped sample.

Reflection spectra (fig. 2) showed that $CaMoO_4$:Bi samples do not contain absorption band in area of 320 nm in contrast with undoped $Ca_{0.98}MoO_4$, which can be associated with the fact that Bi is changing energetic parameters.

3.2 Interband transitions

Results of Kubelka-Munk and Tauc equations were used to understand the dependence between energy gap for direct and indirect electron transitions and concentration of Bi. The spectral dependences of the Kubelka-Munk function in the coordinates for direct and indirect transitions are shown using the example of one of the samples (figure 3, a, b). The approximation of linear range by straight line up to the crossing with the abscissa axis allows determining the energy gap and also

energy of phonons for indirect transitions. Bismuth adding affects energy structure of $CaMoO_4$ which is more expressed for indirect transitions than for direct transitions at lower concentration of dopant (table 1, figure 4).

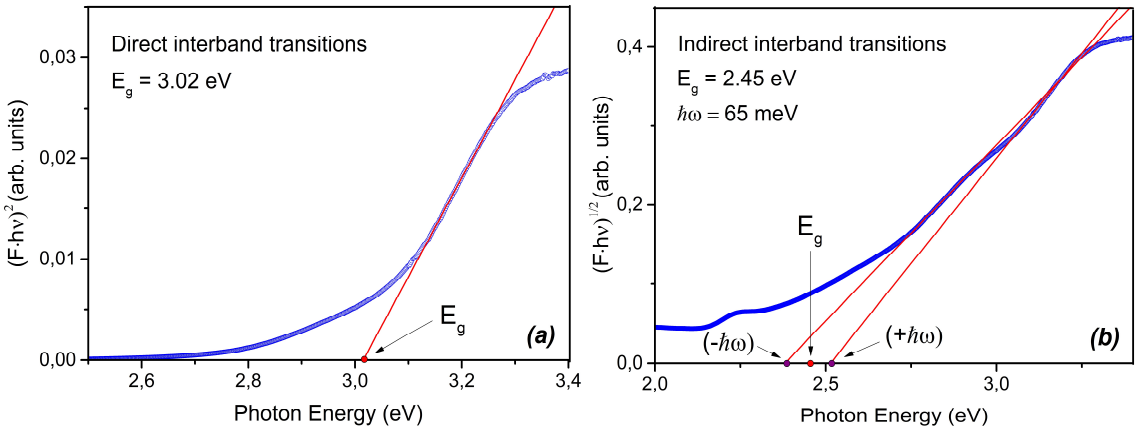

Figure 3 (a,b). Scheme of determination of energy band for direct **(a)** and indirect **(b)** transitions using Tauc equation.

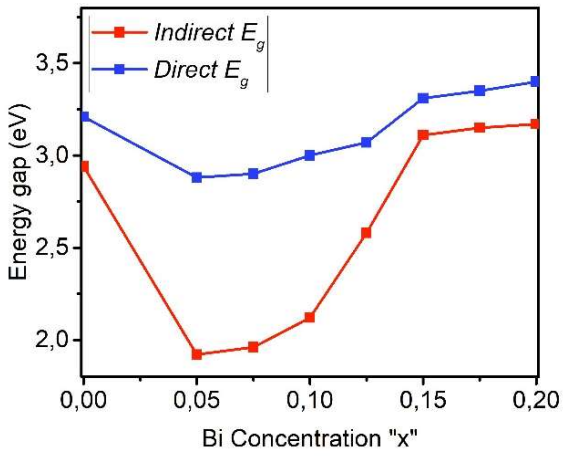

Figure 4. Dependence between energy gap for direct and indirect transitions and dopant concentration.

3.3 Excitation and luminescence spectra

For undoped sample at 4 eV excitation the non-elementary luminescence was observed and can be described as superposition of three gauss bands with maximums at 2.18, 2.45, 2.75 eV (figure 5, a). As showed in [4] non-elementary luminescence can be associated with recombination of self-trapped excitons on anion complex, which are firstly in singlet state and thermally transit to triplet state with lower energy. Singlet energy level is involved to excitation process, while triplet levels are involved to emission due to effective non-radiative relaxation from singlet states to triplet states (figure 5, b).

4. Conclusion

In present work we determining, that adding Bi affects (energy parameters) energy structure of $CaMoO_4$ by changing it is energy gap. At the same time, for indirect transitions this effect is more expressed at lower concentration of dopant, than for direct transitions. Also, this leads to quench of autolocalized excitons luminescence, that was observed for undoped sample.

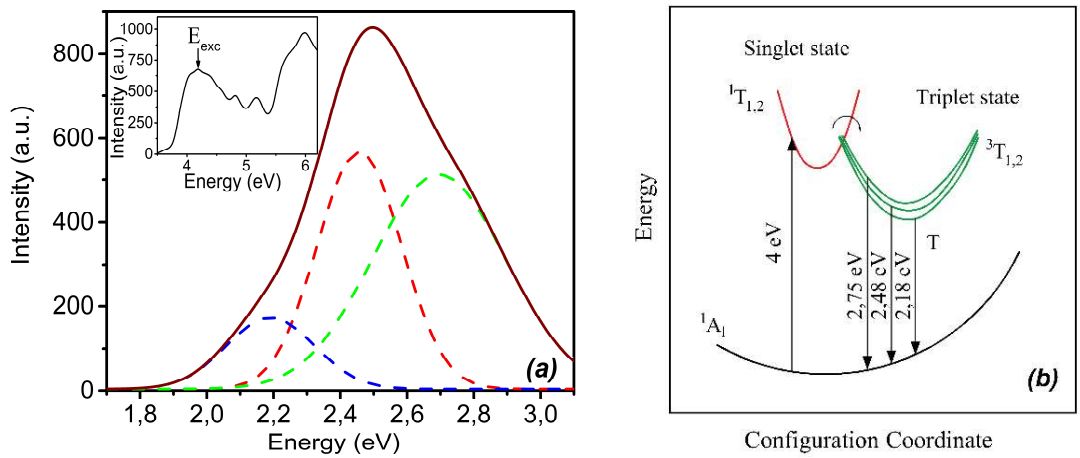

Figure 5 (a, b). (a) Emission and excitation spectra of $Ca_{0,98}MO_4$ with non-elementary luminescence; **(b)** Scheme of radiative transitions in $CaMoO_4$.

Table 1. The energy gap for direct and indirect transitions and phonon energy of materials of $Ca_{1-3x}Bi_{2x}\Phi_xMoO_4$, obtained from analysis of reflection spectra.

	Indirect		**Direct**
Composition	Energy gap, eV	Phonon energy, meV	Energy gap, eV
$Ca_{0.98}MoO_4$	2.94	-	3.21
$Ca_{0.80}Bi_{0.10}MoO_4$	1.92	78	2.88
$Ca_{0.775}Bi_{0.15}MoO_4$	1.96	85	2.90
$Ca_{0.70}Bi_{0.20}MoO_4$	2.12	63	3.00
$Ca_{0.625}Bi_{0.25}MoO_4$	2.58	73	3.07
$Ca_{0,55}Bi_{0,3}MoO_4$	3.11	65	3.31
$Ca_{0,475}Bi_{0,35}MoO_4$	3.15	-	3.35
$Ca_{0,4}Bi_{0,4}MoO_4$	3.17	-	3.4

Acknowledgments
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References
[1] Mikhailik V B, et all 2005 *J. Appl. Phys.* **97** 083523
[2] Kuznetsova Yu A, Zatsepin A F 2017 *J. Phys.: Conf. Ser.* **917** 062001
[3] Kubelka P, Munk F 1931 *J. Tech. Phys.* **12** 593
[4] Mikhailik V B, Kraus H, Itoh M, Iri D, Uchida M 2005 *J. Phys.: Cond. Mat.* **17** 7209